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Melts microheterogeneity in binary metallic systems having eutectic and monotectic transformations

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Abstract. The distinctive features of limited solubility in liquid eutectic and monotectic metallic systems have been discovered. The monodispersed emulsion model has been elaborated for a description of the specific microheterogeneous structure of eutectic melts. It includes the transitional shells (TS) at the interface boundaries having the eutectic composition and the closest packing of atoms. By means of the thermodynamic analysis a possibility of a metastable equilibrium of the emulsion has been determined when dimensional and interface energy parameters of the emulsion adopt certain values. The metastable state is characterized by the colloidal sizes of disperse particles and the interface tension values typical for immiscible melts. The existence of the emulsion has been confirmed by the calorimetric experimental data on Sn-Pb and Al-Si systems. Structure factors and RDF`s of the TS have been calculated by the original treatment of experimental diffraction data on Sn-Pb and Ag-Ge melts. The evidence of different microheterogeneity scales in liquid eutectic and monotectic systems has been obtained. From two immiscible phases only the liquid based on the light-melted metal shows the short-range microinhomogeneity and the second one is a homogeneous solution. So, the microheterogeneity in eutectic and monotectic melts has different nature.

1. Introduction

It is known that binary metallic melts with the eutectic phase diagrams, keep their microheterogeneous state formed during the melting process in wide concentration and temperature intervals. The characteristic dimensional scale of this structure corresponds to colloidal systems [1]. The sizes of the disperse particles (DP) are found to be noticeably larger than the short range order groups of atoms usual in homogeneous solutions. Consequently, the eutectic melts have to contain the clearly expressed interface boundaries in distinction from the true solutions that in their turn may be microscopically inhomogeneous systems. On the opinion of P. Popel [1] these interface boundaries can be a reason of metastable existence of the emulsion for a long time. It destructs under heating, and the melt turns to its stable state of a true solution. The reasons of the emulsion formation and its long stability are discussed but a common view is absent.

The limited solubility of components in the liquid monotectic systems are pronounced more distictly. Some general factors, determining the small solubility in binary metallic systems, are well known. However, there is no clear information on comparing of the liquid state microheterogeneity scales in the systems with the eutectic and monotectic transformations. So, the joint analysis of the structure of these two kinds of melts is expedient.

2. The monodispersed eutectic emulsion model

The model was elaborated for the description of the structure microheterogeneity peculiar to binary eutectic metallic melts [2]. According to this model the melted A-B system after its melting does not turn to the thermodynamically stable true solution state but consists of three liquid phases. They are: the dispersed particles (DP) having identical radius R and containing the component B with the higher melting point (or the saturated B-based solution), the surroundings (S), based on the lower melting point component A (or the saturated A-based solution), and the transitional shells (TS) at the interface boundaries. The TSs are of the eutectic composition and the closest non-crystalline packing of atoms based on Frank-Kasper polyhedrons. The shells are formed due to the strong chemical interaction of components at the contact surface between the solid eutectic phases. The DPs are supposed to be distributed equidistantly at the distance $2D_S$ from each other. A schematic fragment of the model emulsion is shown at the Figure 1.

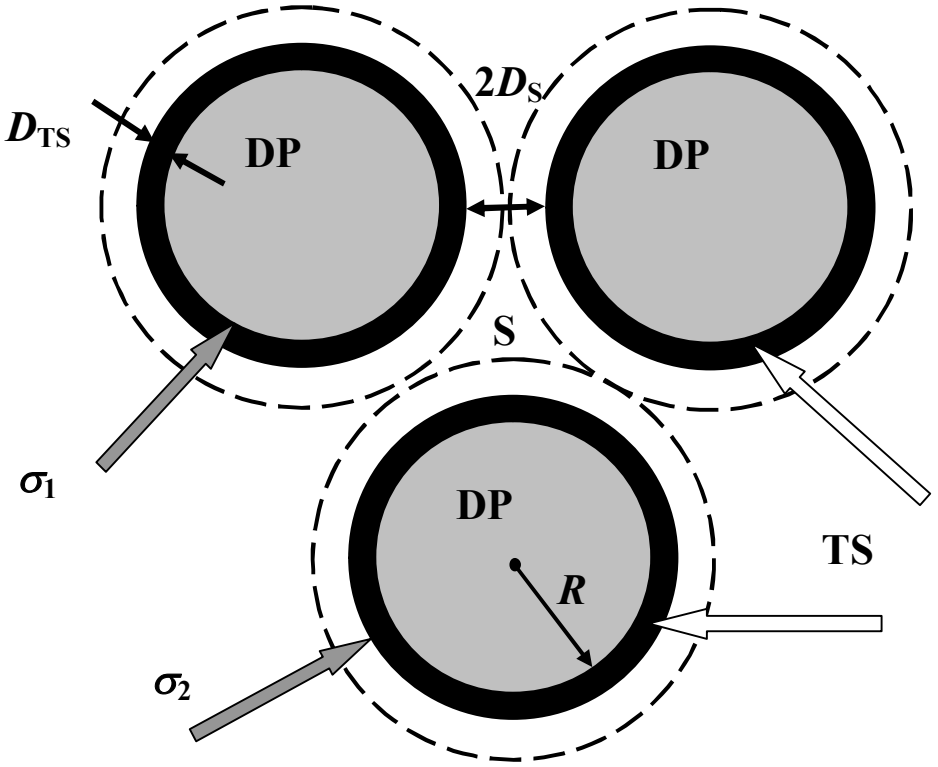

Figure 1. A fragment of the model metastable eutectic emulsion with the equidistantly distributed disperse particles (DP), surrounded by the transitional shell (TS), in the surrounding (S)

According to the model the energy and dimensional characteristics of liquid Sn-Pb and Ag-Ge systems were calculated. The thermodynamic analysis of the model emulsion was carried out [3]. The dependence of the Gibbs energy change at the emulsion formation on the DP radius $\Delta G(R)$ was calculated. It was shown that a minimum can appear in the curve when the radius, the TS thickness D_{TS} and the specific interface energies at the DP-TS (σ_1) and TS-S boundaries (σ_2) are in definite relation. The deepest minimum in both the binary systems corresponds to the smallest DP dimensions of the emulsion that is characterized by the most probable thickness of the TS. The TS thickness was found to be less than 2 to 3 atomic distances and corresponds to the diameter of Frank-Kasper polyhedron. The DP radii corresponding to the minimum were found to be near 1.5 nm and near 15 nm in the Ag-Ge and Sn-Pb melts of eutectic compositions, correspondingly. The authors relate the minimum in the $\Delta G(R)$ dependence to the metastable state of the emulsion. The reduced (to the unit

square of the DP surface) specific interface energy at the minimum increases with *R* growth almost linearly.

The model permits to describe the non-monotonous experimental concentration dependencies of the molar volume of melts under study having a minimum at the eutectic composition. The melt of the eutectic composition was found to be more dispersed than the melts of any other compositions. The TS volume fraction was the highest in this melt.

It is necessary to note that the state of the melt under consideration is not a classic emulsion, which usually forms by two immiscible liquids. In our opinion, the strong atomic interaction at the interface boundaries inherited from the solid state plays a leading role in stability of the dispersion. This interaction lowers the interface tension that stabilizes the emulsion and can be the main reason of the specific dimensional and orientation ratios characteristic to solid eutectics.

The probable mechanism of the emulsion expansion under heating has been proposed. It was based on the experimental dependencies of the melt density on temperature [1]. We assumed that the model emulsion may increase its molar volume at the expense of the TS density decrease. This point of view allows explanation of eutectic microheterogeneity destruction at a temperature when the TS density becomes practically equal to experimental density of the melt. This temperature corresponds to the break point at the density temperature dependence curve, obtained in a heating regime. At this temperature the widened TSs can not stabilize the DPs as regard solution, and the melt turns to its equilibrium true solution state due to a diffusion process.

3. The experimental TSs existence evidence

The presence of the TSs with their specific close packed structure supposed in [4] in eutectic melt has been confirmed [5] by the diffraction data [6] on the discussed binary systems. Assuming that the structure factor (SF) of the eutectic melt near the liquidus may be represented by three SFs, corresponding to DP, S and TS, we have derived the equation, allowing calculation of the SF curve for the TSs. In both the systems these curves demonstrate a decrease of the shortest atomic distances in the TS compared to that in a bulk eutectic solution by 2 to 3 %. According to analysis of the TSs radial distribution functions (RDF) they have a close packed icosahedral structure. These calculation results were found to be in a good agreement with the close packed atomic structure of the TS. The traditional interpretation of the SF and RDF curves does not permit to ascertain the TSs presence in the melt in particular because of their small volume fraction.

The disperse state of the Sn-Pb melts, including the TSs, has been also confirmed by the calorimetric experiments [7]. The temperature dependences of the formation enthalpy change were obtained. The satisfactory coincidence of the experimental and calculated functions has been achieved for the emulsion model but not for the homogeneous solution model.

Thus, we think that the microheterogeneous state of the metallic eutectic melt, formed during the melting process, is the metastable disperse system, kept due to the specific structure of the interface boundaries including the TSs.

4. The atomic structure of liquid immiscible equilibrium phases

For the comparison of the scales of the structure inhomogenites in the eutectic and monotectic metallic systems it was necessary to analyze the RDFs of two immiscible liquids separately from each other. The X-ray diffraction method using a reflected beam gives the interference pattern from the upper liquid phase only. The electron diffraction experiment permits to get the total intensity of scattered electrons for both coexisting liquids. The original method of separation of the two intensity contributions has been proposed [8]. The SF and RDF curves of two liquids L_1 and L_2 have been calculated and simulated for Ga-Bi, Ga-Pb and In-Al systems. The L_1 and L_2 liquids in enumerated systems were found to have dissimilar atomic distributions. The L_1 liquid based on the component with a lower melting point (Ga and In) represents a microheterogeneous solution, where the component with a higher melting point is distributed statistically in the form of clusters with the size not exceeding diameter of one coordination sphere. The structure of the L_2 liquid, which is based on

the component with a higher melting point (Bi, Pb and Al) represents a microscopically homogeneous solution.

In addition, to estimate the reliability of the atomic distributions we have calculated partial fluctuation RDFs $g_{NN}(r)$, $g_{NC}(r)$ and $g_{CC}(r)$ using the Thornton-Bhatia concept. Here r is the atomic distance, $g_{NN}(r)$, $g_{CC}(r)$ and $g_{NC}(r)$ are the partial fluctuation RDFs reflecting fluctuations of density, concentration and mutual density-concentration fluctuations, correspondingly. It is known that, at $r \to \infty$, $g_{NN}(r) \to 1$, $g_{NC}(r) \to 0$, and $g_{CC}(r) \to 0$. It was shown that in our case $g_{CC}(r)$ has no oscillations, reflecting the short-range concentration fluctuations. Their absence confirmed the fact that the L_2 liquid is microhomogeneous.

Thus, apart from a macroscopic separation the discussed systems with the immiscibility gap in a liquid state exhibit the microscopic segregations in only one (L_1) of their two liquid phases.

5. Conclusions

The scale and the structure peculiarities of microheterogeneity of melts in binary eutectic and monotectic metallic systems were found to be sufficiently different. Eutectic alloys heated not too much above the liquidus are not true solutions but the peculiar metastable emulsions. This disperse liquid state has a hereditary nature and depends on the interface periodic structure of the solid eutectic. Both liquid immiscible phases of the monotectic binary systems are true solutions, and only one of them represents the microinhomogeneous distribution of the components. There were not found any physical basis for the specific structure state formation at the interface boundary in monotectic systems.

6. References

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